2 Food Quality and Indices of Failure

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2.1 FOOD QUALITY AND SAFETY

The term "food quality" has a variety of meanings to professionals in the food industry, but the ultimate arbiters of food quality must be the consumers. This notion is embodied in the frequently cited definition of food quality as "the combination of attributes or characteristics of a product that have significance in determining the degree of acceptability of the product to a user." Another definition of food quality is "the acceptance of the perceived characteristics of a product by consumers who are regular users of the product category or those who comprise the market segment." The phrase "perceived characteristics" includes the perception of the food's safety, convenience, cost, value, and so on, and not just its sensory attributes (Cardello, 1998).

For the majority of foods and beverages, quality decreases over time. Therefore it follows that there will be a finite length of time before the product becomes unacceptable. This time from production to unacceptability is referred to as shelf life and was discussed in Chapter 1. Quality loss during storage may be regarded as the result of a form of processing at relatively low temperatures that goes on for rather a long time.

Knowledge of the kinds of changes that influence food quality is the first step in developing food packaging that will minimize undesirable changes in quality and maximize the development and maintenance of desirable properties. Once the nature of the reactions is understood, knowledge of the factors that control the rates of these reactions is necessary in order to minimize the changes occurring in foods during storage, that is, while packaged.

The nature of the deteriorative reactions in foods and the factors that control the rates of these reactions will be briefly outlined. Deteriorative reactions can be enzymic, chemical, physical (typically as a result of moisture gain or loss), and biological (both microbiological and macrobiological, that is, due to insect pests and rodents). Biochemical, chemical, physical, and biological changes occur in foods during processing and storage, and these combine to affect food quality. The most important quality-related changes are (van Boekel, 2008) as follows:

- Chemical reactions, mainly due to either oxidation or nonenzymic browning reactions.
- Microbial reactions: microorganisms can grow in foods. In the case of fermentation this is desired; otherwise, microbial growth will lead to spoilage and, in the case of pathogens, to unsafe food.
- Biochemical reactions: many foods contain endogenous enzymes that can potentially catalyze reactions leading to quality loss (enzymic browning, lipolysis, proteolysis, and more). In the case of fermentation, enzymes can be exploited to improve quality.
- Physical reactions: many foods are heterogeneous and contain particles. These particles are unstable, and phenomena such as coalescence, aggregation, and sedimentation usually lead to quality loss. Also, changes in texture can be considered physical reactions, although the underlying mechanism may be of a chemical nature.

The principal aim of this chapter is to provide a brief overview of the major chemical, biochemical, biological, and physical changes that occur in foods during processing and storage and to show how these combine to affect food quality. Reactions in foods affecting food quality are summarized in Table 2.1. Knowledge of such changes is essential before a sensible choice of packaging materials can be made, as the rate and magnitude of such changes can often be minimized by selection of the correct packaging materials. At the end of the chapter, the concept of indices of failure (IoFs) of food is introduced. IoFs are the quality attributes that will indicate that the food is no longer acceptable to the consumer.

The deterioration of packaged foods (and this includes virtually all foods, because today very few foods are sold without some form of packaging) depends largely on transfers that can occur between the external environment, which is exposed to the hazards of storage and distribution, and the internal environment of the package. For example, there may be transfer of moisture vapor from a humid atmosphere into a dried product, or transfer of an undesirable odor from the external atmosphere into a high-fat product, or development of oxidative rancidity if the package is not an effective oxygen (O_2) barrier. Also, flavor compounds can be absorbed by some types of plastic packaging materials (a phenomenon referred to as scalping), and chemical contaminants can migrate from the packaging material into the food (e.g., plasticizers from plastic film). In addition to the ability of packaging materials to protect and preserve foods by minimizing or preventing the transfers referred to, packaging materials must also protect the product from mechanical damage and prevent or minimize misuse by consumers (including tampering).

Although certain types of deterioration will occur even if there is no transfer of mass (or heat, as some packaging materials can act as efficient insulators against fluctuations in ambient temperatures)

TABLE 2.1
Overview of Reactions in Foods Affecting Quality

Example	Type	Consequences
Nonenzymic browning	Chemical reaction (Maillard reaction)	Color, taste and aroma, nutritive value, formation of toxicologically suspect compounds (acrylamide)
Fat oxidation	Chemical reaction	Loss of essential fatty acids, rancid flavor, formation of toxicologically suspect compounds
Fat oxidation	Biochemical reaction (lipoxygenase)	Off-flavors, mainly due to formation of aldehydes and ketones
Hydrolysis	Chemical reaction	Changes in flavor, vitamin content
Lipolysis	Biochemical reaction (lipase)	Formation of free fatty acids and peptides, bitter taste
Proteolysis	Biochemical reaction (proteases)	Formation of amino acids and peptides, bitter taste, flavor compounds, changes in texture
Enzymic browning	Biochemical reaction of polyphenols	Browning
Separation	Physical reaction	Sedimentation, creaming
Gelation	Combination of chemical and physical reaction	Gel formation, texture changes

Source: Adapted from van Boekel M.A.J.S. 2008. Kinetic modeling of food quality: a critical review. *Comprehensive Reviews in Food Science and Food Safety* 7: 144–158.

between the package and its environment, it is possible in many instances to prolong the shelf life of the food through the use of packaging (Baner and Piringer, 2008).

It is important that food packaging not be considered in isolation from food processing and preservation, or indeed from food marketing and distribution: all interact in a complex way, and concentrating on only one aspect to the detriment of the others is a sure-fire recipe for commercial failure.

The development of an analytical approach to food packaging is strongly recommended, and to achieve this successfully, a good understanding of food safety and quality is required. The more important of these is, without question, food safety, which is the freedom from harmful chemical and microbial contaminants at the time of consumption. Packaging is directly related to food safety in two ways.

First, if the packaging material does not provide a suitable barrier around the food, microorganisms can contaminate the food and make it unsafe. However, microbial contamination can also arise if the packaging material permits the transfer of, for example, moisture or O_2 from the atmosphere into the package. In this situation, microorganisms present in the food but posing no risk because of the initial absence of moisture or O_2 may subsequently be able to grow and present a risk to the consumer.

Second, the migration of potentially toxic compounds from some packaging materials to the food is a possibility in certain situations and gives rise to food safety concerns. In addition, migration of other components from packaging materials, although not harmful to human health, may adversely affect the quality of the product.

The major quality attributes of foods are texture, flavor, color, appearance, and nutritive value, and these attributes can all undergo undesirable changes during processing and storage. With the exception of nutritive value, the changes that can occur in these attributes are readily apparent to the consumer, either before or during consumption. Packaging can affect the rate and magnitude of many of these quality changes. For example, the development of oxidative rancidity can often

be minimized if the package is an effective O_2 barrier; flavor compounds can be absorbed by some plastic polymers but not by others; the particle size of many food powders can increase (i.e., particles can clump) if the package is a poor moisture barrier.

2.2 DETERIORATIVE REACTIONS IN FOODS

Knowledge of the kinds of deteriorative reactions that influence food quality is the first step in developing food packaging that will minimize undesirable changes in quality and maximize the development and maintenance of desirable properties. Once the nature of the reactions is understood, knowledge of the factors that control the rates of these reactions is necessary in order to minimize the changes occurring in foods during storage, that is, while packaged (Robertson, 2006). The nature of the deteriorative reactions in foods is reviewed in this section, and the factors that control the rates of these reactions are discussed in the following section.

Preservation is a means of protecting a product, usually against microbiological deterioration. It is important to understand the differences between biotic deterioration, which refers to changes in a food product brought about either by a biological function (e.g., ripening of fruit, respiration of vegetables) or attack by microorganisms (e.g., molds, bacteria, and yeasts) and abiotic deterioration, which is brought about by physical or chemical agents (e.g., atmospheric O_2, moisture, light, odors, and temperature). Both biotic and abiotic deterioration can lead to food spoilage, albeit by different methods. Packaging can be used to provide a barrier to those agents that lead to deterioration.

Deteriorative reactions in foods are influenced by two factors: the nature of the food and its surroundings. These factors are referred to as intrinsic and extrinsic parameters.

2.2.1 Intrinsic Parameters

Intrinsic parameters are an inherent part of the food and include water activity (a_w), pH, oxidation-reduction potential (E_h), O_2 content, and product formulation, including the presence of any preservatives or antioxidants.

2.2.1.1 Water Activity

The parameter a_w is defined as the ratio of the water vapor pressure of a food to the vapor pressure of pure water at the same temperature. Mathematically:

$$a_w = p/p_o \tag{2.1}$$

where p is the vapor pressure of water exerted by the food and p_o is the saturated vapor pressure of pure water at the same temperature. This concept is related to equilibrium relative humidity (ERH) in that ERH = 100 × a_w. However, whereas a_w is an intrinsic property of the food, ERH is a property of the atmosphere in equilibrium with the food. The a_w of most fresh foods is above 0.99. Every microorganism has a limiting a_w value below which it will not grow, form spores, or produce toxic metabolites.

Water can influence chemical reactivity in different ways. It may act as a reactant (e.g., in the case of sucrose hydrolysis), or as a solvent, where it may exert a dilution effect on the substrates, thus decreasing the reaction rate. Water may also change the mobility of the reactants by affecting the viscosity of the food systems and form hydrogen bonds or complexes with the reacting species. Thus, a very important practical aspect of a_w is controlling undesirable chemical and enzymic reactions that reduce the shelf life of foods. It is a well-known generality that rates of changes in food properties can be minimized or accelerated over widely different values of a_w, as shown in Figure 2.1. Small changes in a_w can result in large changes in reaction rates.

When a food is placed in an environment at a constant temperature and relative humidity (RH), it will eventually come to equilibrium with that environment. The corresponding moisture content

at steady state is referred to as the equilibrium moisture content. When this moisture content (expressed as mass of water per unit mass of dry matter) is plotted against the corresponding RH or a_w at constant temperature, a moisture sorption isotherm results (see Figure 2.2). Such plots are very useful in assessing the stability of foods and selecting effective packaging. As a_w is temperature dependent, it follows that moisture sorption isotherms must also exhibit temperature dependence. Thus, at constant moisture content (which is the situation existing in a food packaged in an impermeable package), a_w increases with increasing temperature. As rates of deteriorative

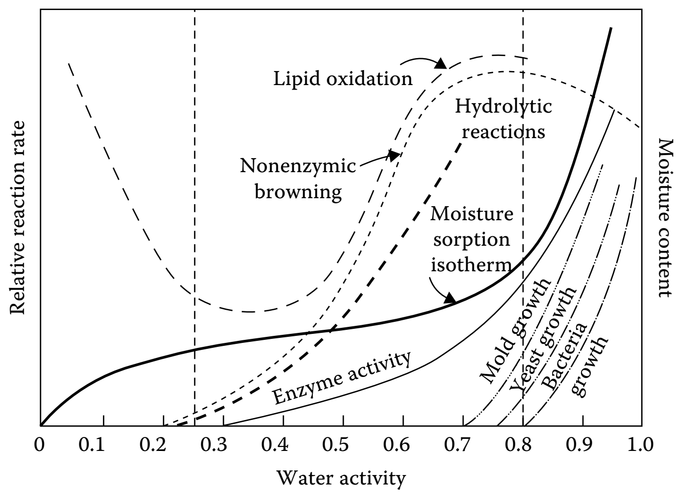

FIGURE 2.1 Rates of reactions as a function of water activity. (Redrawn with permission from Rockland L.B., Beuchat L.R. (Eds). 1987. In: *Water Activity: Theory and Applications to Food*. New York: Marcel Dekker, p. vii. Copyright CRC Press, Boca Raton, Florida.)

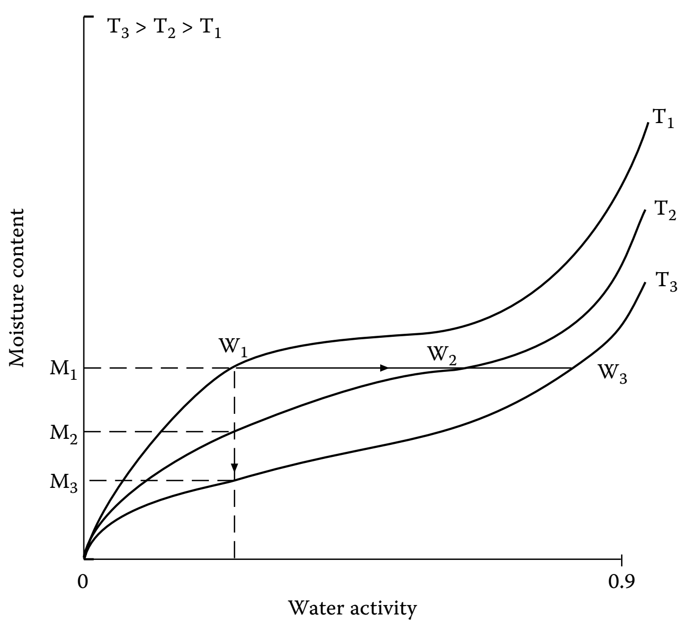

FIGURE 2.2 Schematic of a typical moisture sorption isotherm showing effect of temperature on water activity and moisture content. (From Robertson G.L. 2006. *Food Packaging Principles and Practice*, 2nd edn. Boca Raton, Florida: CRC Press, with permission. Copyright CRC Press, Boca Raton, Florida.)

reactions depend on both a_w and temperature, the increase in rate in such situations will typically be greater than that due solely to an increase in temperature. This has important implications for shelf life.

2.2.1.2 Oxidation-Reduction Potential

The oxidation-reduction potential (also referred to as the redox potential and abbreviated E_h or ORP) is a physicochemical parameter that determines the oxidizing or reducing properties of the medium, and it depends on the composition of the food, pH, temperature, and, to a large extent, the concentration of dissolved O_2 (DO). E_h plays an important role in the cellular physiology of microorganisms, such as growth capacity, enzyme expression, and thermal resistance. Alwazeer et al. (2003) demonstrated that reducing the E_h of orange juice using gas (N_2 and H_2) immediately after heat treatment maximized microbial destruction during pasteurization, prevented the development of microorganisms, and stabilized color and ascorbic acid during storage at 15°C.

The relationship between ORP values and DO levels in milk is not well understood. Several modifications that occur in milk during its processing and storage are driven by different oxidation-reduction reactions. Electrolysis treatments have been applied to milk to produce milk powder with better flavor quality. ORP and DO levels in enriched milk are mainly responsible for the oxidation of unsaturated fatty acids and the loss of viability of probiotic strains such as bifidobacteria. Decreasing the E_h in milk could allow an improvement in the quality of these products. Recent studies on electroreduction of milk by membrane electrolysis have shown that this electrochemical process decreased the E_h of milk without changing the organoleptic and nutritive values (Schreyer et al., 2008).

2.2.2 Extrinsic Parameters

Extrinsic factors that control the rates of deteriorative reactions include temperature, RH, gas atmosphere, and light; packaging can, to varying degrees, influence the impact of these factors on the rates of deteriorative reactions, depending on the specific packaging material.

2.2.2.1 Temperature

Temperature is a key factor in determining the rates of deteriorative reactions, and in certain situations the packaging material can affect the temperature of the food. This is particularly so with packaging materials that have insulating properties, and these types of packages are typically used for chilled and frozen foods. For packages that are stored in refrigerated display cabinets, most of the cooling takes place by conduction and convection. Simultaneously, there is a heat input by radiation from the fluorescent lamps used for lighting. Under these conditions, aluminum foil offers real advantages because of its high reflectivity and high conductivity.

Several models have been developed to represent the effect of temperature on the rates of deteriorative reactions.

2.2.2.1.1 Linear Model

This simple expression relating the rate of reactions and temperature has been used for many years:

$$k = k_o \mathrm{e}^{b(T-T_o)} \tag{2.2}$$

where

k_o = rate at temperature T_o (°C)
k = rate at temperature T (°C)
b = a constant characteristic of the reaction
e = 2.7183.

2.2.2.1.2 Arrhenius Relationship

The most common and generally valid relationship for the effect of temperature on the rates of deteriorative reactions is that of Arrhenius. The relationship in the integrated form is

$$k = k_o e^{-E_a/RT} \tag{2.3}$$

where
- k = rate constant for deteriorative reaction
- k_o = constant, independent of temperature (also known as the Arrhenius, pre-exponential, collision, or frequency factor)
- E_a = activation energy (J mol^{-1})
- R = ideal gas constant (8.314 J K^{-1} mol^{-1})
- T = absolute temperature (K)

The integrated relationship contains the inherent assumption that the activation energy and the pre-exponential factor do not change with temperature. Although this assumption is generally true, it is not universally so, and predictions based on this model sometimes fail when applied over a temperature span of greater than ~40°C. Furthermore, when the reaction mechanism changes with temperature, the activation energy may vary substantially. The value of E_a is a measure of the temperature sensitivity of the reaction, that is, how much faster the reaction will proceed if the temperature is raised. The activation energy depends on factors such as a_w, moisture content, solids concentration, and pH.

2.2.2.1.3 Temperature Quotient

Another term used to describe the response of biological systems to temperature change is the Q value, a quotient indicating how much more rapidly the reaction proceeds at temperature T_2 than at a lower temperature T_1. If Q reflects the change in rate for a 10°C rise in temperature, it is then called Q_{10}. Mathematically:

$$Q_{10} = \frac{k_{T+10}}{k_T} \tag{2.4}$$

It can be shown that the rate of a deteriorative reaction at two temperatures is related to the shelf life θ at those two temperatures; that is:

$$k_T \theta_{s(T)} = k_{T+10} \theta_{s(T+10)} \tag{2.5}$$

where
- $\theta_{s(T)}$ = shelf life at temperature T°C
- $\theta_{s(T+10)}$ = shelf life at temperature $(T + 10)$°C

Therefore,

$$Q_{10} = \frac{\theta_{s(T)}}{\theta_{s(T+10)}} \tag{2.6}$$

If the temperature difference is Δ rather than 10°C, the following equation can be used:

$$\left(Q_{10}\right)^{\Delta/10} = \frac{\theta_{s(T1)}}{\theta_{s(T2)}} \tag{2.7}$$

For example, if the Q_{10} for the key deteriorative reaction was 3 and the shelf life θ_s at 37°C was 4 months, then the shelf life at 23°C would be

$$\theta_{23} = \theta_{37} \times (Q_{10})^{\Delta/10} = 4 \times (3)^{14/10} = 18.6 \text{ months} \tag{2.8}$$

If, however, the Q_{10} was 2 rather than 3, then

$$\theta_{23} = \theta_{37} \times (Q_{10})^{\Delta/10} = 4 \times (2)^{14/10} = 10.5 \text{ months} \tag{2.9}$$

This example illustrates the importance of having an accurate estimate of Q_{10}.

It can be shown when the Arrhenius model is used that

$$\ln Q_{10} \approx \frac{10E_a}{RT^2} \tag{2.10}$$

Note that Q_{10} is not constant but depends on both the E_a and the temperature; when Q_{10} is reported, the temperature range over which it applies should also be specified.

2.2.2.2 Relative Humidity

The RH of the ambient environment is important and can influence the a_w of the food unless the package provides an excellent barrier to water vapor. Many flexible plastic packaging materials provide good moisture barriers, but none is completely impermeable, thus limiting the shelf life of low a_w foods.

2.2.2.3 Gas Atmosphere

The presence and concentration of gases in the environment surrounding the food have a considerable influence on the growth of microorganisms, and the atmosphere inside the package is often modified. The simplest way of modifying the atmosphere is vacuum packaging, that is, removal of air (and thus O_2) from a package prior to sealing; it can have a beneficial effect by preventing the growth of aerobic microorganisms. Flushing the inside of the package with a gas such as CO_2 or N_2 before sealing is the basis of modified atmosphere packaging (MAP). For example, increased concentrations of gases such as CO_2 are used to retard microbial growth and thus extend the shelf life of foods. MAP is increasing in importance, especially with the packaging of fresh fruits and vegetables, flesh foods, and bakery products.

Atmospheric O_2 generally has a detrimental effect on the nutritive quality of foods, and it is therefore desirable to maintain many types of foods at a low O_2 tension, or at least prevent a continuous supply of O_2 into the package. Lipid oxidation results in the formation of hydroperoxides, peroxides, and epoxides, which will, in turn, oxidize or otherwise react with carotenoids, tocopherols, and ascorbic acid to cause loss of vitamin activity.

With the exception of respiring fruits and vegetables and some flesh foods, changes in the gas atmosphere of packaged foods depend largely on the nature of the package. Adequately sealed metal and glass containers effectively prevent the interchange of gases between the food and the atmosphere. With flexible packaging, however, the diffusion of gases depends not only on the effectiveness of the closure but also on the permeability of the packaging material, which depends primarily on the physicochemical structure of the barrier.

2.2.2.4 Light

Many deteriorative changes in the nutritional quality of foods are initiated or accelerated by light. Light is, essentially, an electromagnetic vibration in the wavelength range between 4000 and 7000 Å; the wavelength of ultraviolet (UV) light ranges between 2000 and 4000 Å. The catalytic effects of light are most pronounced in the lower wavelengths of the visible spectrum and in the UV

spectrum. The intensity of light and the length of exposure are significant factors in the production of discoloration and flavor defects in packaged foods.

Modification of plastic materials can be achieved by incorporation of dyes or application of coatings that absorb light at specific wavelengths. Recently nano-sized particles of titanium dioxide have been incorporated into plastic films to absorb UVA and UVB rays. Glass is frequently modified by inclusion of color-producing agents or by application of coatings. In this way a wide range of light transmission characteristics can be achieved in packages made of the same basic material.

There have been many studies demonstrating the effect of packaging materials with different light-screening properties on the rates of deteriorative reactions in foods. Among the most commonly studied foods has been fluid milk, the extent of off-flavor development being related to the exposure interval, strength of light, and amount of milk surface exposed.

2.2.3 Enzymic Reactions

From a food packaging point of view, knowledge of enzyme action is essential to a fuller understanding of the implications of different forms of packaging. The importance of enzymes to the food processor is often determined by the conditions prevailing within and outside the food. Control of these conditions is necessary to control enzymic activity during food processing and storage. The major factors useful in controlling enzyme activity are temperature, a_w, pH, chemicals that can inhibit enzyme action, alteration of substrates, alteration of products, and preprocessing control.

Three of these factors are particularly relevant in a packaging context. The first is temperature: the ability of a package to maintain a low product temperature and thus retard enzyme action will often increase product shelf life. The second important factor is a_w, because the rate of enzyme activity is dependent on the amount of water available; low levels of water can severely restrict enzymic activities and even alter the pattern of activity. Finally, alteration of substrate (in particular, the ingress of O_2 into a package) is important in many O_2-dependent reactions that are catalyzed by enzymes, for example, enzymic browning due to oxidation of phenols in fruits and vegetables.

2.2.4 Chemical Reactions

Many of the chemical reactions that occur in foods can lead to deterioration in food quality (both nutritional and sensory) or the impairment of food safety. Such reaction classes can involve different reactants or substrates, depending on the specific food and the particular conditions for processing or storage. The rates of these chemical reactions are dependent on a variety of factors amenable to control by packaging, including light, O_2 concentration, temperature, and a_w. Therefore, the package can, in certain circumstances, play a major role in controlling these factors, and thus indirectly the rate of the deteriorative chemical reactions.

The two major chemical changes that occur during the processing and storage of foods and lead to a deterioration in sensory quality are lipid oxidation and nonenzymic browning (NEB). Chemical reactions are also responsible for changes in the color and flavor of foods during processing and storage.

2.2.4.1 Lipid Oxidation

Autoxidation is the reaction of molecular O_2 by a free radical mechanism with hydrocarbons and other compounds. The reaction of free radicals with O_2 is extremely rapid, and many mechanisms for initiation of free radical reactions have been described. The crucial role that autoxidation plays in the development of undesirable flavors and aromas in foods is well documented, and autoxidation is a major cause of food deterioration.

Factors that influence the rate and course of oxidation of lipids are well known and include light, local O_2 concentration, high temperature, the presence of catalysts (generally transition metals such as iron and copper, but also heme pigments in muscle foods), and a_w. Control of these factors can significantly reduce the extent of lipid oxidation in foods.

2.2.4.2 Nonenzymic Browning

Nonenzymic browning (NEB) is one of the major deteriorative chemical reactions that occur during storage of dried and concentrated foods. The NEB, or Maillard, reaction can be divided into three stages: (1) early Maillard reactions involving a simple condensation between an aldehyde (usually a reducing sugar) and an amine (usually a protein or amino acid) without browning; (2) advanced Maillard reactions that lead to the formation of volatile or soluble substances; and (3) final Maillard reactions leading to insoluble brown polymers.

2.2.4.3 Color Changes

Acceptability of color in a given food is influenced by many factors, including cultural, geographical, and sociological aspects of the population. However, regardless of these many factors, certain food groups are acceptable only if they fall within a certain color range. The color of many foods is due to the presence of natural pigments such as chlorophylls, anthocyanins, carotenoids, flavonoids, and myoglobin.

2.2.4.4 Flavor Changes

In fruits and vegetables, enzymically generated compounds derived from long-chain fatty acids play an extremely important role in the formation of characteristic flavors. In addition, these types of reactions can lead to important off-flavors. Enzyme-induced oxidative breakdown of unsaturated fatty acids occurs extensively in plant tissues, and this yields characteristic aromas associated with some ripening fruits and disrupted tissues (Lindsay, 2008).

Fats and oils are notorious for their role in the development of off-flavors through autoxidation. Aldehydes and ketones are the main volatiles from autoxidation, and these compounds can cause painty, fatty, metallic, papery, and candlelike flavors in foods when their concentrations are sufficiently high. However, many of the desirable flavors of cooked and processed foods derive from modest concentrations of these compounds. The permeability of packaging materials is of importance in retaining desirable volatile components within packages and in preventing undesirable components entering the package from the ambient atmosphere.

2.2.4.5 Nutritional Changes

In addition to the chemical changes described earlier, which may have a deleterious effect on the sensory properties of foods, there are other chemical changes that can affect the nutritive value of foods. The four major factors that influence nutrient degradation and can be controlled to varying extents by packaging are light, O_2 concentration, temperature, and a_w. However, because of the diverse nature of the various nutrients as well as the chemical heterogeneity within each class of compounds and the complex interactions of these variables, generalizations about nutrient degradation in foods are unhelpful.

2.2.5 Physical Changes

The physical properties of foods can be defined as those properties that lend themselves to description and quantification by physical rather than chemical means and include geometrical, thermal, optical, mechanical, rheological, electrical, and hydrodynamic properties. Geometrical properties encompass the parameters of size, shape, volume, density, and surface area as related to homogeneous food units, as well as geometrical texture characteristics. Although many of these physical properties are important and must be considered in the design and operation of a successful

packaging system, in the present context the focus is on undesirable physical changes in packaged foods.

The major undesirable change in food powders is the sorption of moisture as a consequence of an inadequate barrier provided by the package, resulting in caking. This can occur as a result either of poor selection of packaging material in the first place or of failure of the package integrity during storage. Caking or spontaneous agglomeration of food powders (especially those containing soluble components or fats) occurs when they are exposed to moist atmospheres or elevated storage temperatures. The phenomenon can result in anything from small soft aggregates that break easily to rock-hard lumps of variable size to solidification of the whole powder. For foods containing solid carbohydrates, the greatest effect in physical properties results from sorption of water; such changes can occur in boiled sweets (leading to stickiness or graining) and milk powders (leading to caking and lumpiness).

2.2.6 Microbiological Changes

Microorganisms can make both desirable and undesirable changes to the quality of foods, depending on whether they are introduced as an essential part of the food preservation process (e.g., as inocula in food fermentations) or arise adventitiously and subsequently grow to produce food spoilage. In the latter case, they reach readily observable proportions only when they are present in the food in large numbers. As the initial population or microbial load is usually small, observable levels are reached only after extensive multiplication of the microorganisms in the food.

The two major groups of microorganisms found in foods are bacteria and fungi, the latter consisting of yeasts and molds. Bacteria are generally the fastest growing, so in conditions favorable to both, bacteria will usually outgrow fungi. The phases through which the two groups pass are broadly similar: a period of adjustment or adaptation (known as the lag phase) is followed by accelerating growth until a steady, rapid rate (known as the logarithmic phase, because growth is exponential) is achieved. After a time the growth rate slows until growth and death are balanced and the population remains constant (known as the stationary phase). Eventually, death exceeds growth and the organisms enter the phase of decline.

The species of microorganisms that cause the spoilage of particular foods are influenced by two factors: the nature of the foods and their surroundings. These factors are referred to as intrinsic and extrinsic parameters and were discussed earlier.

Every microorganism has a limiting a_w value below which it will not grow, form spores, or produce toxic metabolites. Water activity can influence each of the four main growth cycle phases by its effect on the germination time, the length of the lag phase and the growth rate phase, the size of the stationary population, and the subsequent death rate. Generally, reducing the a_w of a given food increases the lag period and decreases the growth rate during the logarithmic phase, the maximum of which becomes lower.

Whether a microorganism survives or dies in a low a_w environment is influenced by intrinsic factors that are also responsible for its growth at higher a_w. These factors include water-binding properties, nutritive potential, pH, E_h, and the presence of antimicrobial compounds. Microbial growth and survival are not entirely ascribed to reduced a_w but are also attributable to the nature of the solute. Key extrinsic factors relating to a_w that influence microbial deterioration in foods include temperature, O_2, and chemical treatments. These factors can combine in a complex way to encourage or discourage microbial growth.

Microbiological changes due to the growth of microorganisms are desirable in fermentation but are mostly undesirable in other environments, because microbial growth may lead to spoilage and even health-threatening situations when pathogens come into play. The ability to predict growth of bacteria in foods is very important in predicting shelf life. A frequently used growth model is the modified Gompertz model, which is discussed in Chapter 4.

The temperature of storage is particularly important, and several food preservation techniques (e.g., chilling) rely on reducing the temperature of the food to extend its shelf life. Although there

is a very wide range of temperatures over which the growth of microorganisms has been reported (–34°C to 90°C), specific microorganisms have relatively narrow temperature ranges over which growth is possible. Molds are able to grow over a wider range of temperature than bacteria, with many being capable of growth at refrigerator temperatures.

The presence and concentration of gases in the environment has a considerable influence on the growth of microorganisms. Most food pathogens do not grow at refrigerator temperatures, and CO_2 is not highly effective at nonrefrigeration temperatures. Therefore, most MAP food is usually held under refrigeration. Temperature abuse of the product (i.e., holding at nonrefrigerated temperatures) could allow the growth of organisms (including pathogens) that were inhibited by CO_2 during storage at lower temperatures. For these reasons, it is difficult to evaluate MAP safety solely on the growth of certain pathogens at abusive temperatures.

2.3 RATES OF DETERIORATIVE REACTIONS

As discussed in the preceding section, a number of deteriorative chemical, biochemical, physical, and microbiological reactions can occur in foods. The rates of these reactions depend on both intrinsic (compositional) and extrinsic (environmental) factors. As well as understanding the nature of these reactions, it is important to have an appreciation of their rates, so that they can be controlled. Control of deteriorative reactions requires a quantitative analysis based on knowledge of the kinetics of food deterioration. Fortunately, simple chemical kinetics can be applied to such reactions.

Quantitative analysis of the deteriorative reactions that occur in a food during processing and storage requires the existence of a measurable index of deterioration (IoD), that is, a chemical, physical, or sensory measurement or set of measurements that may be used reproducibly to assess the changes occurring. An increase or decrease in the IoD must correlate with changes in food quality. For quantitative analysis of quality changes, the IoD must be expressed as a function of the conditions existing during processing and storage so that the changes can be predicted or simulated. Thus, calculation of quality losses requires a mathematical model that expresses the effect of intrinsic and extrinsic factors on the IoD.

The general equation describing quality loss may be written as

$$-\mathrm{d}D/\mathrm{d}\theta = f(I_i, E_j) \tag{2.11}$$

where

$-\mathrm{d}D/\mathrm{d}\theta$ = rate of change of some index of deterioration D with time θ; a negative sign is used if the concentration of D decreases with time

I_i = intrinsic factors ($i = 1 \ldots m$)

E_j = extrinsic factors ($j = 1 \ldots n$)

As the quality of foods and the rate of quality changes during processing and storage depend on intrinsic factors, it is possible in many cases to correlate quality losses with the loss of a particular component such as a vitamin or pigment. The conversion of a single component or quality factor C to an end-product G (e.g., conversion of chlorophyll to pheophytin, or conversion of ascorbic acid to brown pigments) may be written as:

$$D \rightarrow \text{intermediate products} \rightarrow G \tag{2.12}$$

The absolute concentrations of D or G need not be measured. For example, the production of brown pigments in foods is often measured as the increase in absorbance at 420 nm of an alcoholic extract of the food, and the change in absorbance is used as an indicator of the extent of the reaction. Such

quality loss can be represented as being proportional to the power of the concentration of the reactant or product:

$$-dD/d\theta = kD^n \quad (2.13)$$

or

$$dG/d\theta = kG^n \quad (2.14)$$

where

D and *G* = concentration of index of deterioration or quality factor
θ = time
k = rate constant (dependent on extrinsic factors)
n = a power factor called the order of the reaction that defines whether the rate is dependent on the concentration of *D* or *G*. The value of *n* can be a fraction or a whole number
$dD/d\theta$ and $dG/d\theta$ = change in concentration of *D* or *G* with time

Equation 2.14 implies that extrinsic parameters such as temperature, a_w, and light intensity are held constant; if they are not, then their influence on the rate constant *k* must be taken into account in evaluating the equation.

For most deteriorative reactions in foods, the reaction order *n* has generally been shown to be either 0 or 1, that is, a zero- or first-order reaction. Typical pseudo-zero-order deteriorative reactions include nonenzymic browning (e.g., in dry cereals and powdered dairy products), lipid oxidation (e.g., development of rancidity in snack foods, dry foods, and frozen foods), and enzymic degradation (e.g., in fresh fruits and vegetables, some frozen foods, and some refrigerated doughs). Typical pseudo-first-order deteriorative reactions also include nonenzymic browning (e.g., loss of protein quality in dry foods), lipid oxidation (e.g., development of rancidity in salad oils and dry vegetables), vitamin loss in canned and dry foods, and microbial production of off-flavors and slime in flesh foods.

From a packaging point of view, it is often useful to know the concentration of *D* or *G* at which the product is no longer acceptable, for example, when the concentration of a vitamin or pigment has fallen below some level (e.g., 50% reduction in concentration) or the concentration of some undesirable brown color has risen above some level. In these situations, the shelf life of the food (θ_s) is the time for the concentration of *D* (or *G*) to reach an undesirable or critical level (D_c or G_c). Examples showing the application of these equations to shelf life calculations can be found in Robertson (2006).

2.4 INDICES OF FAILURE

In designing suitable packaging for foods, it is important first to define the indices of failure (IoFs) of the food, that is, the quality attributes that will indicate that the food is no longer acceptable to the consumer. These may or may not be the same as the IoDs. An IoF could be development of rancid flavors in cereals due to oxidation, loss of red color (bloom) in chilled beef due to depletion of O_2, reduction of carbonation in bottled soda due to permeation of CO_2 through the bottle wall, caking of instant coffee due to moisture ingress, development of microbial taint in chilled poultry, or moisture loss in green vegetables resulting in wilting.

Once the IoFs for a particular food have been defined, the next step is to attempt to quantify the magnitude of the particular degradation, for example, how much moisture or O_2 can react with the food before it becomes unacceptable. The final step is to ascertain which (if any) of the IoFs might be influenced by the packaging material, as packaging cannot prevent all deteriorative reactions in foods. If, for example, the IoF of a snack food was loss of crispness, then the packaging material

could influence this by the extent to which it permitted the ingress of moisture. Different plastic films, for example, have different water vapor transmission rates and, thus, the shelf life obtained varies depending on the particular plastic selected. Similar considerations apply to foods for which the IoF is oxidation, as different packaging materials have different O_2 transmission rates (OTRs).

However, it is not just the packaging material itself that can influence shelf life; the method of filling the product into the package is also important. For example, with roasted and ground coffee, vacuum filling into metal cans will remove 95% or more of the O_2 from the can compared with inert gas flush packing in plastic foil laminate pouches, which will remove or displace 80–90% of the O_2 in the package. The residual O_2 in the package at the time of filling will have a major influence on shelf life regardless of the O_2 barrier properties of the package itself.

In the chapters that follow, the IoFs for particular foods are described, and ways in which they can be influenced by packaging are outlined.

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